PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improved Rubber Compounds based on Blends of Polyethylene and Polybutadiene and their application

We, THE INTERNATIONAL SYNTHETIC RUBBER COMPANY LIMITED, a company organised under the laws of Great Britain, of Brunswick House, Brunswick Place, Southampton, Hampshire, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved rubber compositions suitable for use, for example, in tyre tread stock, and in particular to the blending of polyethylene with polybutadiene, in the presence or absence of other elastomers, which blends exhibit improvements in physical properties and processing as compared to polybutadiene alone.

Compositions have already been described wherein up to 10 parts by weight, per hundred parts rubber, of a low molecular weight polyethylene are incorporated in a rubber, to act as a lubricant. The polyethylene used in the process of the present invention differs from that previously employed in that it is a high molecular weight polymer having a melt flow index of 1—30 (British Standards 2782—1962, Method 105C). Thus the polyethylene used is of the type normally used in moulding. The present invention applies equally to polyethylene of low or high density and any of the normal commercial methods may be used to prepare the polyethylene.

The polybutadiene used in this invention is stereo-specific polybutadiene. Such a stereospecific polybutadiene may be obtained by the solution polymerisation of butadiene in the presence of stereospecific catalysts such as lithium alkyls, and contains monomeric units of cis 1,4, trans 1,4, and 1,2 addition, the cis 1,4 units comprising at least 30% and up to 98% by weight of the total weight of the polymer. Any other convenient method may be used to prepare the stereo-specific polybutadiene. Preferably the molecular weight of the polybutadiene is in the range from 15,000—300,000.

In its most general concept, the present invention provides a rubber composition including at least 10 parts by weight of stereospecific polybutadiene and, optionally, up to 90 parts by weight of a second elastomer, based on the total 100 parts by weight of elastomers, and at least 5% of a high molecular weight polyethylene having a melt flow index of 1—30, based on the total polyethylene/polybutadiene loading.

More particularly, a rubber composition according to the present invention includes a stereospecific polybutadiene, having a cis 1,4 addition structure of between 30% and 98%, by weight, based on the total weight of polymer, and from 5% to 25% of a high molecular weight polyethylene, having a melt flow index of 1—30, based on the total polyethylene/polybutadiene loading.

In a second preferred form the present invention provides a rubber composition comprising from 10—90 parts by weight of stereospecific polybutadiene having a cis 1,4 addition structure of between 30% and 98% by weight, based on the total weight of polymer, blended with from 90—10 parts by weight of a second elastomer, based on the total weight of elastomers, and from 5% to [illegible]% by weight of a high molecular weight polyethylene, having a melt flow index of 1—30, based on the total polyethylene/polybutadiene loading. Therefore, when 50:50 and 75:25 blends of elastomer/polybutadiene are used, 90% polyethylene based on the polyethylene/polybutadiene loading, is

equivalent to 31% and 18.4% respectively of polyethylene based on total polymer weight (polybutadiene plus elastomer plus polyethylene).

The preferred amount of polyethylene incorporated in the rubber is from 15—25%, based on the polyethylene/polybutadiene loading.

Examples of suitable second elastomers which may be blended with the stereospecific polybutadiene are styrenebutadiene copolymers and natural rubber.

The polybutadiene, and other elastomer if present, can be extended with an aromatic oil without loss of the improved physical properties resulting from the presence of the polyethylene. The loading of oil may be up to 60 or 70 parts by weight per 100 parts by weight of polybutadiene and other elastomer, if present.

The blending may be carried out in any convenient manner which will uniformly distribute the polyethylene through the polybutadiene and other elastomer, i.e. in a conventional internal (Banbury) mixer.

The improvements in physical properties occur particularly in vulcanisable and vulcanised rubber compounds containing the polyethylene/polybutadiene composition of the invention and carbon black and/or mineral fillers and vulcanising ingredients. The vulcanisable and vulcanised rubber compounds have the following improved properties compared with conventional recipes:—

(a) High wet skid resistance of tyres resulting from higher hysteresis.
(b) Higher tear resistance.
(c) Less abrasion loss.
(d) Better ozone resistance.
(e) Increased hardness without loss in mould flow properties.
(f) Lower mixing temperature.
(g) Faster extrusion speeds.
(h) Improved calendering characteristics.
(i) A better control of uncured dimensional changes (die swell and shrinkage).
(j) The possibility of incorporating larger quantities of polyethylene without loss in hardness or general physical properties.
(k) Improved surface finish of extrudates, mouldings and calendered sheet.
(l) The rheological properties of the unvulcanised compound make it ideal for injection moulding.

The following examples and data illustrate the improved properties of the rubber compounds based on and including the polyethylene/polybutadiene composition of the present invention. The amounts of substances given are parts by weight. The polybutadiene used in these examples was "Intene" (Intene is a Registered Trade Mark). The approximate stereo configuration of this polymer is 55% trans 1,4, 35% cis 1,4 and the remainder 1,2. The polyethylene used had a Melt Index of 4.5—5.5.

EXAMPLE I

Composition	A	B
Polybutadiene	40	20
Polyethylene	—	20
Styrene-butadiene copolymer	60	60
Intermediate super abrasion furnace black	52	52
Aromatic oil	12	12
Zinc oxide	4	4
Stearic acid	1.6	1.6
Cyclohexylbenzthiazylsulphenamide	1.2	1.0
Sulphur	1.4	1.2
N-phenyl-N'-isopropyl-p-phenylene diamine	1.2	1.2

After vulcanisation the compounds exhibited the following properties:

Property	A	B
(a) Wet skid resistance	100	109
(b) Die swell	+38.2%	−19.8%
(c) Mixing Temperature	300°F.	270°F.
(d) Hardness	63(IRHD)	77(IRHD)
(e) Mooney Plasticity (ML_4 at 100°C)	44	52
(f) Extrusion speed (using a Garvey die)	487 g/min	536 g/min

The figures for (a) were obtained using the skid resistance tester developed by the Road Research Laboratory which has been shown to give reliable correltion with actual tyre tests. (Sarback, Hallman and Brunot — Rubber Age 1965 Vol. 97 No. 4 Pages 76—79).

From these results it can be seen that replacing 20 parts of polybutadiene by 20 parts of the polyethylene in compound B resulted in a higher wet skid resistance and increased hardness without moulding difficulty, and a lower mixing temperature and faster extrusion speed.

EXAMPLE II

Composition	C	D
Polybutadiene	100	100
Polyethylene	20	30
Aromatic oil	20	30
High abrasion furnace black	50	75
Zinc oxide	5	5
Stearic acid	2	2
Cyclohexylbenzthiazylsulphenamide	1.5	1.5
Sulphur	1.5	1.5

Property	C	D
(a) Hardness (cured)	72.5	74
(b) Tensile Strength (psi) (cured)	1600	1650
(c) Cost Comparison Index	100	95.5

This example shows the effect of increasing the quantity of oil incorporated in the polybutadiene together with the amount of polyethylene, thus giving cheaper compounds. Whereas addition of oil to polybutadiene alone results in a softening of the rubber, the reverse occurs in the above example: D which has the higher oil and polyethylene content has both a greater hardness and greater tensile strength.

EXAMPLE III

Composition	E	F
Polybutadiene	50	40
Polyethylene	—	10
Styrene-butadiene copolymer	50	50
Fine particle silica	50	50
Naphthenic oil	15	15
Polyethylene glycol	1.5	1.5
Zinc oxide	5	5
Stearic acid	2	2
Sulphur	2	2
Mercaptobenzthiazole	1.5	1.5
Diphenyl guanidine	1	1

Property	E	F
(a) Abrasion Index (cured)	100	127
(b) Tear Index (cured)	100	115

Compounds B, D and F when compared with A, C and E also show better calendering characteristics, improved surface finish or extrudates, mouldings and calendered sheet, and improved ozone resistance.

A further experiment was carried out using a commercially available high cis 1,4 polybutadiene. The amounts of polymers and vulcanising ingredients as set out in Example I(B) were employed and the results obtained were almost identical. Thus both low cis polybutadiene and high cis polybutadiene can be treated according to the present invention, with equal success.

Tyre Test

Test tyres were made incorporating tread segments of 1) a conventional high hysteresis tread compound containing 50 p.h.r. black and based on a "high styrene" oil extended styrene-butadiene rubber 2) a tread compound containing 50 p.h.r. black and based on a 1:3:4 blend of polyethylene/polybutadiene/oil extended styrene-butadiene rubber. These two compounds had equivalent hardness (61°B.S.) and the following physical properties:—

	(1)	(2)
Tensile Strength (psi)	3064	2400
Elongation at Break (%)	380	570
Resilience at 20°C.	44.2	49.8
Wet Skid Resistance	72	69

These test tyres were run on a test route using standard tyre test techniques and an abrasion index was calculated. Compound 1) had an abrasion index of 92.7 as compared with 100 for Compound 2).

These tests showed that the compound incorporating polyethylene with polybutadiene had an improved wear rate when compared with a conventional high hysteresis tread stock.

A direct comparison between SBR/polybutadiene blends with and without polyethylene has shown that blends without polyethylene have an abrasion index of greater than 100 but that the wet skid resistance of the blend, 66, is notably poorer than that for blends including polyethylene.

It is well known that SBR/polybutadiene blends usually give tyre treads which have wet skid characteristics which are inferior to those of tread compounds based on SBR alone. From the results set out above it can been seen that whilst the wet skid resistance of the tread including polyethylene is still not quite so high as that for the tread based on SBR alone, it is, nevertheless, higher than that for straight SBR/polybutadiene blends.

Ozone Tests

These were carried out on various compounds based on blends of SBR/polybutadiene in the ratio 4:3 with various amounts of polyethylene. Results obtained were as follows using 50 p.p.h.m. ozone at 38°C. (No antiozonant present).

No. of p.h.r. polyethylene	0	10	15	25
Hours to appearance to first crack	4	13	17	25

Thus a substantial increase in ozone resistance is obtained even with only 10 p.h.r. polyethylene.

WHAT WE CLAIM IS:

1. A rubber composition including at least 10 parts by weight of stereospecific polybutadiene and optionally up to 90 parts by weight of a second elastomer, based on the total 100 parts by weight of elastomers, and at least 5% of a high molecular weight polyethylene having a melt flow index of 1—30, based on the total polyethylene/polybutadiene loading.

2. A rubber composition including a stereospecific polybutadiene having a cis 1,4 addition structure of between 30% and 98%, by weight based on the total weight of polymer, and from 5% to 25% of a high molecular weight polyethylene, having a melt flow index of 1—30, based on the total polyethylene/polybutadiene loading.

3. A rubber composition including from 10 to 90 parts by weight of stereospecific polybutadiene having a cis 1,4 addition structure of between 30 and 98% by weight, based on the total weight of polymer, blended with from 90—10 parts by weight of a second elastomer, based on the total weight of elastomers, and from 5% to 90% by weight of a high molecular weight polyethylene, having a melt flow index of 1—30, based on the total polyethylene/polybutadiene loading.

4. A rubber composition according to claims 1 or 3 wherein the second elastomer is a styrene-butadiene copolymer or natural rubber.

5. A rubber composition according to any preceding claim wherein the molecular weight of the stereospecific polybutadiene is in the range from 15,000 to 300,000.

6. A rubber composition according to any preceding claim including up to 70 parts by weight of an aromatic oil, per 100 parts by weight of elastomers.

7. A rubber composition according to any preceding claim including mineral fillers.

8. A rubber composition according to any preceding claim including carbon black.

9. A rubber composition according to any preceding claim including vulcanising ingredients.

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